



## TECHNIQUES IN ADVANCING THE CAPABILITIES OF VARIOUS NITRATE DETECTION METHODS: A REVIEW

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*Abstract- Strategies to facilitate detection enhancement in various methods of nitrate detection are presented in this paper. The main nitrate detection methods for the past 10 years will be reviewed according to their advantages and disadvantages, followed by a focus on the techniques on increasing detection capabilities. For each detection method, an investigation of the technique of improvement is carried out. The utilisation of advance material such as membranes, reduction agents etc. is also identified as the key aspect for system improvement. Many researchers in the field of potentiometry, electrochemical, and biosensors have focused on miniaturising their detection systems to enhance the capability of nitrate in-situ measurement. The performance of miniaturised sensor systems is comparable to that of conventional systems.*

**Index terms:** Nitrate; Selective Membrane; Planar Electromagnetic Sensor; Review and Detection

## I. INTRODUCTION

Living organisms need water for survival. Water pollution is due to the presence of pollutants such as nitrate, phosphate, and heavy metal ions. The World Health Organisation (WHO) has restricted the allowable level of nitrate in drinking water at most 10 mg/L. Nitrate ions are an important and commonly occurring nitrogen species in the environment. Nitrate intake (at low concentrations) has several positive aspects such as improving blood flow, reducing blood pressure, cardio, and vasoprotective effect. However, there are many consequences on human health due to consuming high concentrations of nitrate, particularly in drinking water, such as gastric cancer and Parkinson's disease. Nitrate can trigger illness on infant such as "blue baby syndrome" or known as methemoglobinemia [1]. Meanwhile, in animal farming industries, nitrate poisoning can lead to livestock abortions and low dairy yields. Hence, it could result in large losses to farmers. Nitrate in aquatic system stimulates the production of algae and phytoplankton. Overproduction of algae and phytoplankton leads to eutrophication, where the growth of algae and phytoplankton explodes in polluted water. Much oxygen is required for decomposition process of algae and phytoplankton when they die. Therefore, aquatic life suffers and finally dies. The source of nitrate basically comes from anthropogenic activities such as industry, agriculture, sewage, livestock, and discharge of domestic wastewater, which raised the level of toxic contaminants in water [2]. The future direction of ion nitrate detection enhancement capabilities can be reviewed from the perspective of selectivity membranes or materials, sensor design and configuration, electrode materials, bonding improvement between membrane and electrodes, and minimising the environmental impact.

Presently, membrane technology has received great attention for pollutant removal in water. The characteristics of the membrane, such as high adsorption capacities and low cost, make it suitable to be integrated into sensor technology to enhance the selectivity towards targeted ions [3]. The selection of membrane material is crucial in order to produce a highly selective system. Many studies have proposed several types of membrane in the nitrate ion detection system. The material that is used as a membrane is modified silica polymer dope, doped polypyrrole, zinc (II) complex polymeric membrane [4], and trihexyltetradecyl-phosphonium chloride polymeric

membrane [5]. Currently, research on the improvement and innovation of membranes for pollutant detection is still ongoing.

Another aspect that can be improved in the nitrate detection system is the bonding condition between membrane and electrodes when it comes to the sensor that is associated with membrane technology. Generally, bonding condition will determine the performance of the sensor, especially the selectivity towards the targeted ions. Furthermore, weak bonding conditions make the sensor non-durable for long usage. In all instances, dip coating is a technique that is introduced to attach the membrane onto the electrode surface [3]. This technique provides a strong bonding condition with homogeneous coated surface. The advantage of this technique is that the thickness of the membrane can be controlled by adjusting the coating speed. Hence, the dip coating technique is crucial to be used as the alternative to obtain a strong bonding condition and smooth coating surface.

Currently, many sensor designs that utilise electrodes reconfiguration have been introduced for environmental monitoring. Such sensors are electromagnetic sensors based on meander and interdigital sensors. Modelling and design optimisation of the sensors help to improve their sensitivity. For example, the inductance of an electromagnetic sensor is highly dependent on the dimension of the outer and inner diameters of the meander sensor. Hence, the total impedances of the electromagnetic sensor will change according to the sensor configuration and therefore lead to sensitivity changes. As a result, many workers have invented new configurations of sensors with high sensitivity [6,7].

Various types of materials have been used as the sensing element for environmental monitoring. Among them are copper [6], gold [8], silver [9], and platinum [10]. Generally, these materials exhibit good conductivity. Among these materials, the gold-based electrode sensor is a popular choice for pollutant detection as it has the ability to attract nitrate ions [6]. Hence, it increases sensor selectivity. Furthermore, gold-based sensors can solve the corrosion issue facing copper-based sensors, as gold is an anti-corrosion material.

Environmental impacts such as temperature, vibration, other pollutants'/ions' presence in the analyte etc., will affect the measurement precision. This environmental impact may come from natural sources or via industrial and experimental waste. Therefore, it is crucial to control the measurement conditions in order to obtain reliable data. Several methods have been introduced to overcome this problem. These can be achieved by using reducing agents and miniaturisation of

the sensor system. Reducing agents have been introduced for noise suppression. Hence, it improved the measurement precision. Meanwhile, miniaturisation of the sensor system such as lab-on-chip (LOC) is an alternative method to reduce the amount of sample used for measurement. Therefore, a less hazardous element of the sample or experimental waste would be released into the environment. Furthermore, the LOC concept provides advantages such as fewer by-products and becoming easier to manage. In this paper, the overall objective is to review the current technology of nitrate ion detection, with an emphasis on capability enhancement. This paper provides a representative survey of the scientific literature, such as strategies to facilitate detection enhancement in various methods of nitrate detection.

## II. CONVENTIONAL DETECTION STRATEGIES

Nitrate detection methods are classified into two types: direct and indirect methods [11]. Indirect methods reported in [6] are expensive as many components are required. Furthermore, the procedure for the measurement using indirect methods is complicated, requiring extra reagents. Among the examples of indirect methods are reduction of nitrate ions into ammonium, nitrite gas followed by gasometry [12], determination of nitrate via vanadium (III) chloride [13], spectrophotometric [14], and UV resonance Raman spectroscopy [15]. As reported in [12], most indirect methods are time-consuming, require control of the working/reaction condition, suffer from interference by other ions and are not feasible for small quantities of nitrate measurement. Meanwhile, direct methods such as biosensors [16], chromatography [17], and potentiometry [18] provide an economical method for detection. The most popular direct method is potentiometry [6,12]. Unfortunately, interference from contaminants in water that leads to measurement error is the problem faced by most direct methods [19]. An overview of advantages as well as disadvantages of the conventional methods for nitrate detection is provided in Table 1.

Table 1: Overview of conventional methods for nitrate detection

Detection methods	Advantages	Ref.	Disadvantages	Ref.
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Potentiometry	* Low cost * Simple monitoring instrument	[12,18]	* Measurement error due to interference from other contaminants	[11]
Electrochemical	*Low cost *Simplicity * High sensitivity and selectivity	[9]	* Kinetic charge transfer at electrode surface are low thus direct reduction of nitrate is characterised by poor sensitivity and reproducibility	[26]
Ion Chromatography	*Short response time *Good reproducibility, *High sensitivity	[17]	* Low sample throughput and large scale equipment	[2]
Biosensor	*Broad detection range, low limit of detection (LOD), highly stable system and high sensitivity	[16]	* Limitation of large sample size required	[27]

### III. POTENTIOMETRY SYSTEM

Potentiometry was introduced in late 1976 for nitrate ion detection in water. This system can be used as a direct detection method; thus it does not require any additional reagents. In the last decade, the field has undergone a renaissance, and the performance of ISEs has dramatically improved in terms of selectivity and detection limit. Many improvements have been made in order to improve the system performance. Such improvement of this system takes place by integration with ion-selective electrodes (ISEs). Hence, by using this system, the free ion concentration in water can be directly determined. The advantages of this technique are its low cost, non-destruction of sample, portable device, and the requirement of minimum sample pre-treatment. Research of the potentiometry system has followed several avenues. Early work by Hassan [11] was concerned with organic nitrate ions and nitramine determination based on the reaction with mercury sulphuric acid mixture. Mendoza *et. al.* [20] characterised a nanobiocomposite as Ion Selective Electrodes (ISE) for nitrate ion determination in water.

Mahajan *et. al.* [4] developed a polymeric membrane by means of Zn (II) complex-based electrodes that work as anion carriers for nitrate anion determination in water. Li [21] and Nuñez [22] predict the nitrate contamination level in water based on an artificial neural network (ANN) algorithm. Table 2 summarises the potentiometry system with limit of detection (LOD). Meanwhile, Table 3 summarises the advantages and disadvantages of the system.

Table 2: LOD of potentiometric system and types of working electrode and membranes

Ref.	Working electrode and membrane	Reference electrode	Limit of Detection (LOD)	Nernstian slope (mV/dec)	Application
[12]	Silver bis (bathophenanthroline and plasticized polyvinyl chloride)	Ag/AgCl	0.05 µgm/L	-55.1 ± 0.1	Nitrate detection in wastewater, fertiliser and pharmaceuticals
[22]	Graphite-epoxy and polyvinyl chloride	Ag/AgCl	4.6 µmol/L	-68.2	Monitoring of photoelectrocatalytic treatment of nitrate
[24]	Nitrate polymeric, tetraoctylammonium nitrate, tris (2-ethylhexyl), polyvinyl chloride and tetrahydrofuran	Ag/AgCl	9.56 mg/L	-59.5	Nitrate and potassium monitoring in water recycling process
[18]	Glassy carbon electrode (GCE) and nitrate doped polypyrrole (PPy(NO <sub>3</sub> -))	Ag/AgCl	10-4.8 mol/L	-55.1 ± 1.1	Soil macronutrient monitoring
[18]	Glassy carbon electrode (GCE), graphite and tetraoctylammonium nitrate	Ag/AgCl	10-5.2 mol/L	-57.4 ± 0.8	Soil macronutrient monitoring
[20]	Graphite-epoxy and chitosan/bentonite	Ag/AgCl	2 × 10 <sup>-4</sup> . M	-54.6	Nitrate determination in water
[5]	Platinum wire and trihexyltetradecylphosphonium chloride (THTDPCl) polymeric membrane	Ag/AgCl	2.8 × 10 <sup>-6</sup> . mol/L	-60.1	Nitrate determination in water
[23]	Graphite electrode and doped polypyrrole	Silver wire	1 × 10 <sup>-5</sup> . M	-54-55	Nitrate determination
[4]	PVC, plasticiser, NaTPB and Zn(II) complex	Ag/AgCl	1 × 10 <sup>-5</sup> . M	-55.16	Selective determination of nitrate anion

Table 3: Advantages and disadvantages of potentiometry system

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>*High sensitivity towards targeted ions [60,61]</li> <li>*Hardly pollutes environmental samples [21,62]</li> <li>*Simple fabrication procedure [12,23]</li> <li>*Simple monitoring instrument/in field detection [12,18,64]</li> <li>*Simple design architecture/construction [12,24]</li> <li>*Simple operation for direct determination of nitrate [18,61]</li> <li>*Mass production [12]</li> <li>*Fast response/feedback system [18,21,61,62,64]</li> <li>*High selectivity towards targeted ion [12,61]</li> <li>*Low-cost system [12,18,20,61]</li> <li>*Easy handling system for online/in-situ measurement [18,20,62]</li> <li>*Accurate measurement [20]</li> </ul>	<ul style="list-style-type: none"> <li>*Poor repeatability system [1]</li> <li>*Maintenance for reconditioning and fresh solution is required after long period of detection [18]</li> <li>*Lack of selectivity [63]</li> <li>*Large error caused by logarithmic response [65]</li> <li>*Measurement error due to interference from other contamination [2]</li> <li>*Temperature-dependent system [60]</li> <li>*Influence solution changes [60]</li> <li>*Adsorption of solution components on membrane surface hence affect nature of charge transfer [3]</li> <li>*Need additional components such as IC for signal amplification as voltage potential depends on analyte concentration</li> </ul>

The use of a membrane helps the potentiometry system to be selective to nitrate ions and is one of the factors that affects the system's limit of detection (LOD). Bendikov and Harmon [23] mentioned that doped polypyrrole (PPy(NO<sub>3</sub><sup>-</sup>)) is a highly selective membrane in an ISE system for nitrate determination in water. They revealed that conductive polymer polypyrrole is widely used due to its high conductivity ability and it being relatively stable. As a result, Zhang *et al.* [18] took the initiative to apply doped polypyrrole as a sensitive membrane material for the potentiometry system. The polypyrrole could improve selectivity, simplify the recipe procedure, and reduce toxicity compared to the conventional non-porous polyvinyl chloride (PVC) ISE [18]. Moreover, this study successfully demonstrated that the use of carbon nanostructure materials between the membrane and the substrate layer in the electrode structure of potentiometric system could prevent the water formation that led to instability. Meanwhile,



Mahajan *et. al.* [4] developed a polymeric membrane that was made of zinc (II) complex for selective nitrate determination in water. The finding demonstrates that the output of a potentiometry system using zinc (II) complex membrane exhibits better selectivity for nitrate ions than for other inorganic anions. They highlighted the advantages of zinc (II) complexes, such as stable detection reproducibility and being highly sensitive to nitrate. Wardak [5] developed an active membrane component using trihexyltetradecylphosphonium chloride (THTDPCI) for polymeric membrane. THTDPCI could enhance the PVC membrane sensitivity by reducing electrical resistance.

The majority of potentiometric nitrate sensors that integrated either true-liquid or liquid polymeric membranes are bulky due to the tubular design with internal reference electrode and internal reference electrolyte solutions. Thus, a micro-fabricated planar potentiometric sensor was introduced [12,24]. The micro-scale sensor could provide several advantages such as small size, simple design, low cost and mass production. Various materials are introduced to produce a micro-scale potentiometric sensor chip. Such materials are screen-printed thick film, silicon transducer chip, silicon nitride base chip and metal printed flexible polyimide film. Current miniaturised micro scale sensors for nitrate detection demonstrate a good response towards nitrate ions.

The miniaturisation of ISEs, while maintaining their selectivity and sensitivity, is a crucial step in the next phase of ISE evolution. Traditionally, in so-called coated-wire ISEs, the ion-selective membrane is placed directly on a solid electronically conductive support, thereby removing the need for an inner solution. However, in these devices, it was observed that the long-term potential stability was quite limited, and they were useful only in specific applications such as capillary electrophoresis or in flow-injection analysis. An important breakthrough in ISE design was achieved by the application of conducting polymers (CPs) as a solid contact layer, i.e. a mediating layer between the electronically conducting substrate and ionically conducting ISE membrane, which was possible due to the mixed conductivity of CPs. Various conductive polymers have been examined as possible internal contact materials that could simultaneously stabilise the overall electrode potential and remove the need for an inner filling solution.

Basically, the conventional architecture of the system consists of two electrodes known as the working electrode and the reference electrode; a salt bridge, and a voltmeter. Figure 1(a)



illustrates the architecture of the conventional potentiometry system. Meanwhile Figure 1(b) illustrates that of the miniaturised potentiometry system.

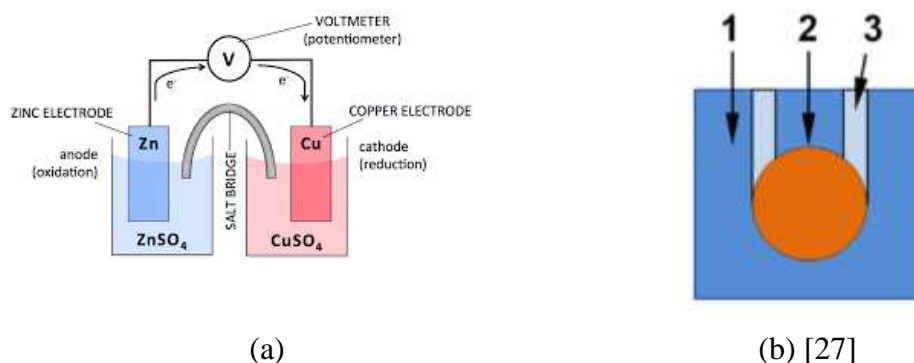


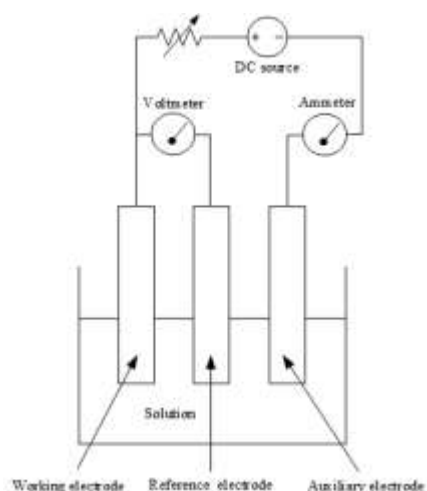
Figure 1: (a) Architecture of the conventional potentiometry system and (b) Miniaturised potentiometry system (1) ceramic layer; (2) epoxy-graphite composite and polymeric membrane; (3) microfluidic channel

#### IV. ELECTROCHEMICAL SYSTEM

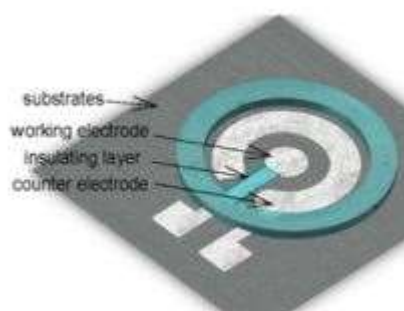
The electrochemical detection of nitrate and nitrite can be divided into a number of categories. Fortunately, these can be broadly grouped within the distinctions of voltammetric and potentiometric systems. Electrochemical systems have the ability to convert the measurement of nitrite ions into the current signal, potential difference and impedance, respectively. In electrochemical systems, various types of electrode were introduced for nitrate detection. Such electrodes are copper, silver, platinum, Glassy carbon electrode (GCE), Graphite-epoxy and chitosan/bentonite, and Silver bis (bathophenanthroline and plasticized polyvinyl chloride). The material's performance is evaluated by its sensitivity and LOD. Table 4 summarises the system performance based on different types of material. According to Table 4, different materials have affected the electrochemical system's performance.

The electrochemical method is widely used due to its high sensitivity to nitrate, simple operation, easy to miniaturise and low power-consumption. However, the conventional electrochemical cell is too massive to be a portable and durable device. Research into electrochemical systems for nitrate detection has followed several avenues [25–27]. This is due to the demand for portable devices for continuous monitoring of nitrate concentration in aqueous solutions. Hence,

analytical systems need to be highly miniaturised and sensitive enough to nitrate over long periods of time. The miniaturised analytical devices and their applications are an important topic in modern analytical chemistry. The portability of the miniaturised system can be used especially for applications outside the laboratory environment in order to overcome drawbacks of convention analytical procedures, which commonly involve the collection of a sample at one location and then a delay while the sample is sent to the laboratory, processed and analysed in the laboratory. Several researchers have developed a microfluidic base associated with electrochemical sensors for miniaturisation and portable purposes [28–30]. This combination has promoted many advantages such as the small configuration of electrodes that can be integrated within a microfluidic platform, requiring a minimum instrumentation, small volume of sample, fast response time, and low cost. Moreover miniaturised electrochemical detection is reliable, selective, and highly sensitive to the measured sample. The current architecture of miniaturised electrochemical sensor is designed based on the planar form or flatten of structure. The performance of miniaturised electrochemical sensor demonstrated good LOD that is comparable to the conventional size of electrochemical system. Figure 2(a) illustrates the conventional electrochemical system architecture. Meanwhile, Figure 2(b) illustrates the miniaturised electrochemical system architecture.



(a)



(b) [39]

Figure 2(a) Architecture of conventional electrochemical system; and (b) Miniaturised electrochemical system

In an electrochemical sensor system, sensitive materials are crucial in order to determine the presence of nitrate in the analyte solution. [29] categorised sensitive materials based on their properties: biocatalysts, organic conducting polymer and metal electrocatalysts. Metal catalysts such as copper, silver, and palladium offer enhancement in terms of sensitivity and selectivity for nitrate detection in analyte solution. Furthermore, the fabrication of metal catalysts is simple and reproducible. Hence, electrocatalysts have been widely used as sensitive materials. On the other hand, a conducting polymer dope such as polypyrrole is expensive and has to be stored in the dark during the polymerisation process, which has limited its application [26]. Moreover, biocatalysts such as nitrate reductase enzymes are too sophisticated to be used [30]. The selection of sensitive materials to be used in electrochemical system is one of the factors that affect the system's LOD. Table 5 summarises the main advantages and disadvantages of electrochemical systems.

Table 4: LOD of electrochemical/Amperometric/Voltametric system and types of working, counter and reference electrode and application

Ref.	Working electrode and membrane	Counter electrode	Reference electrode	Limit of Detection (LOD)	Application
[56]	Glassy carbon electrode (GCE) and polypyrrole-coated palladium nanoclusters	Glassy carbon electrode (GCE) and polypyrrole-coated palladium nanoclusters	Glassy carbon electrode (GCE) and polypyrrole-coated palladium nanoclusters	0.7444–1.5117 $\mu\text{M}$	Nitrate detection at pH 7.0
[29]	Platinum deposited with copper layer	Platinum deposited with copper layer	Saturated calomel electrode (SCE)	0.1 mg/L	Total nitrogen (TN) determination in fresh water
[30]	Platinum deposited with copper layer	Platinum deposited with	Saturated calomel	5 $\mu\text{mol/L}$	Nitrate determination in

		copper layer	electrode (SCE)		fresh water
[28]	Platinum microelectrode	Planar platinum microelectrode	Ag/AgCl	10 $\mu\text{mol/L}$	Nitrate detection at pH 2.0
[27]	Glassy carbon	Platinum wire	Ag/AgCl	0.17 mM	Nitrate measurement in phosphate buffer solution (PBS) at pH 7.5
[66]	PTFE-shrouded copper disk electrode	Platinum wire	Ag/AgCl	1.7–3.0 $\mu\text{M}$	Nitrate determination in low concentration solution at pH 3
[9]	Silver (Ag)-ultramicroelectrodes (UMEs)	Platinum wire	Ag/AgCl	3.2–5.1 $\mu\text{M}$	Nitrate detection in real environmental water samples
[67]	Graphene modify copper electrode	Platinum wire	Ag/AgCl	10 $\mu\text{M}$	Nitrate detection in alkaline media
[68]	Copper-micro electrode array	Platinum wire	Ag/AgCl	1.8 $\mu\text{mol/L}$	Nitrate detection in water
[69]	Palladium electrode	Copper electrode	Saturated calomel electrode	3.6 mg/L	Nitrate ion monitoring in natural water
[70]	Carbon paste electrode (CPE)	Pt-wire	Ag/AgCl	0.009 $\mu\text{M}$	Nitrate and nitrite analysis using microfluidic device
[71]	Copper wire	Platinum wire	Ag/AgCl	11 $\mu\text{M/L}$	Nitrate determination in mineral water

Table 5: Advantages and disadvantages of electrochemical/amperometric/voltametric system

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"> <li>* High sensitivity towards targeted ions [29,30,56,66,68,72]</li> <li>* Less power consumption during operation [28,30]</li> <li>* Simple operation for direct determination of nitrate [29,30,68]</li> <li>* High selectivity towards targeted ions [30,56]</li> <li>* Fast response/feedback system [66,67]</li> <li>* Suitable for in situ/on line analyses [30,66]</li> <li>* Viable approach for portable application as relatively simple [30,56]</li> <li>* Low-cost system [56,68]</li> <li>* Small and compact system [29,30]</li> </ul>	<ul style="list-style-type: none"> <li>* Surface cumulative passivation effect [28]</li> <li>* Complicated programmed potential protocol for renewal of microelectrode surface/electrode re-activation [28]</li> <li>* Extensive procedure for reagent preparation [27]</li> <li>* Measurement result is influenced by other contamination in analyte solution/samples [26]</li> <li>* Tedious reagent preparation procedure [27]</li> <li>* Sensitive materials such as doped polypyrrole need to be stored in the dark during polymerisation [26,29]</li> <li>* Sensitive materials such as doped polypyrrole are expensive [29,30]</li> <li>* Sensitive materials such as nitrate reductase enzymes are too sophisticated to be field-deployable [29,30]</li> <li>* Interference of other ions in water such as chloride, sulphate and phosphate [26]</li> <li>* Requirement of different types of material for the electrode in the system such as working, counter and reference electrode [27,67]</li> </ul>

## V. CHROMATOGRAPHY SYSTEM

Chromatography refers to a laboratory technique used for mixture separation specifically in chemical separation components where the anion or cation of the analyte sample is extracted based on the reaction with the eluent. The chromatography technique is very important in chemical analysis and bioanalysis. Several types of chromatography have been introduced for pollutant detection; namely, high-performance liquid chromatography (HPLC) [31], ionic chromatography [32], and ultra-performance liquid chromatography (UPLC) [33]. Ion chromatography is widely used to analyse nitrate in water [2,34]. . An ion chromatography system consists of solvent, solvent degasser, pump, injector, filter, pre-column heat exchanger, guard column, column, thermostatted compartment, post-column heat exchanger, electrolytic

suppressor and detector. Table 6 summarises the types, eluent, detector, LOD and application of chromatography system for nitrate detection. However, the system is expensive and bulky, which has restricted its application for in-situ measurement. Chromatography systems can be used with different types of detector to detect the presence of nitrate in an analyte solution.

Chromatography detection systems include simple UV, fluorimetric, electron capture, electrochemical and mass spectroscopic [2,17,31-37]. The popularity of UV detection lies in the simplicity of the approach and the ability to attenuate the detection wavelength. The low absorbance of most inorganic ions helps to maintain a low background from which nitrite and nitrate can be resolved. However, the aromatic eluents typically used in anion exchange tend to give rise to high background UV absorbance, complicating the direct detection of nitrate/nitrite. An illustration of ion chromatography system architecture is shown in Figure 3.

Many workers have introduced new methods in order to improve the system performance [31,34,37]. A novel method based on HPLC for nitrate and nitrite determination in water has been developed [31]. The method is simple, sensitive, and selective towards nitrate and nitrite ions. It is based on ion exchange separation and photochemical reaction. Niedzielski et al. [34] introduced a new method using ion chromatography for the simultaneous determination of inorganic nitrogen species such as nitrate, nitrite and ammonium ions in a water sample. This method proposes an ion exchange method for ion separation and an optical detection system for ion detection using UV-vis diode-array. Zuo et al. [37] developed a simple, fast, accurate and highly sensitive ion-pair HPLC method based on direct spectrophotometric detection for nitrate and nitrite ion determination in lake water. This method proposes spectrophotometric detection due to the ability of the detection to generate high selectivity and sensitivity for nitrate and nitrite measurement.

Conventional chromatography systems are always bulky in size. Since microfluidic technology was introduced, many workers have applied this technology to miniaturise the chromatography system. Several detection methods have been applied to this miniaturised chromatography system. Such detection methods are UV detection, fluorescence, and electrochemical detection. The evolution of bulky chromatography systems to miniaturised systems has provided several advantages such as reduced system size, reduced analyte consumption, higher throughput, less time-consuming, and cheap mass production. However, no research has focused on nitrate detection using miniaturised chromatography.

Table 6: Chromatography types, eluent, detector, LOD and application

Ref.	Chromatography types	Eluent	Detector	LOD	Application
[34]	Ion chromatography	Sodium chloride	UV-vis diode array	0.05 mg/L	Nitrate, nitrite and ammonium ion, detection in rain water samples
[2]	Ion chromatography	Sodium hydroxide	Amperometry and absorbance	6 µg/L	Nitrate and bromide detection in water
[31]	High-performance liquid chromatography (HPLC)	Borate buffer (pH 10.0)	Luminolchemiluminescence	$1.0 \times 10^{-11}$ M	Nitrite and nitrate determination in water
[37]	High-performance liquid chromatography (HPLC)	Tetrabutylammonium hydroxide, sodium phosphate (pH 3.9), and acetonitrile	UV light	5 µg/L	Nitrate and nitrite determination in dew, rain, snow and lake water samples
[35]	Liquid chromatography	Toluene and sodium hydroxide	Fluorescence	0.3 pg/L	Low level of nitrate determination in biological, food and environmental monitoring

Table 7: Advantages and disadvantages of chromatography system

Advantages	Disadvantages
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<ul style="list-style-type: none"> <li>* High sensitivity towards targeted ions [2,31,35,37]</li> <li>*High selectivity towards targeted ions [31,35]</li> <li>*Accurate measurement/analysis [2,37]</li> <li>*Fast nitrate determination/analysis [2,34,37]</li> </ul>	<ul style="list-style-type: none"> <li>*Bulky and not portable [2,31,34]</li> <li>*Sample pre-treatment is required [2,31,36]</li> <li>*Expensive instrument</li> </ul>
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## VI. BIOSENSOR SYSTEM

A biosensor is one of the direct methods used for nitrate detection in water. In a biosensor system, the concentration of targeted ion in an analyte solution can be determined by employing the biological material, detection system and signal conditioning circuit. The analyte solution is directly exposed to a biological material. The biological material interacts with the targeted ion in the analyte solution. Information on the interaction process is then translated into an electrical signal such as voltage or current by a detection system. The signal is harvested by the signal conditioning circuit in the biosensor system. The signal conditioning circuit such as a digital data acquisition system will recondition the acquired data before being analysed. The concentration of nitrate ion is estimated based on the output signal of the proposed detection system.

Over the last decade, the miniaturisation of biosensor system has been carried out to characterise and quantify the bio molecules. The reduction size of the sensor system can promote lower material cost, lower the power consumption and the system weight. Hence, the biosensor system demand in the marketplace has increased. Businesses are measuring devices that incorporate a biological sensing element in conjunction with a transducer, yielding a useful signal for measurement and control. Biosensors also have been playing a major role in medicine, food safety, bioprocessing, environmental, and industrial monitoring. Interactions between biological systems and electronic systems are intended to achieve a new revolution in the life sciences and healthcare. In most biosensors and also chemical and gas sensors, the trace of detection reversible redox species should be implemented by using very small amounts of samples, to descend upon the nanolitre or picolitre range. Here, the conventional photolithography technique is used for the

fabrication of micro-gap electrodes on silicon substrate and employed as an electrochemical microelectrode sensor for measuring pH.

Nitrate biosensors have been developed over the last two decades considering the advantage of enzymes that are strongly substrate-selective. Nitrate reductase (NR) is used in the fabrication of nitrate biosensors. However, its multiredox centre responsible for the biological conversion of nitrate to nitrite is generally not very active, and is deeply embedded in the protein structure, thus preventing the direct electron transfer with the electrode.

Carbon nanotubes (CNTs) have emerged as a new class of nanomaterials that are receiving considerable interest owing to their ability to promote electron transfer reactions with enzymes showing low electroactivity. The high conductivity of this carbon material has led to improving electrochemical signal transduction, while its nano architecture imposes an electron contact between the redox centres. CNTs can donate and accept electrons in a wide range of potentials, and could therefore be used as mediators in biosensor systems. As a result, [27] investigated the performance of carbon nanotube/Polypyrrole/Nitrate reductase biofilm electrodes for nitrate detection.

Table 8 summarises the different types of biological material, detection systems, LOD and applications of biosensor systems for nitrate ion detection. Meanwhile, Table 9 summarises the advantages and disadvantages of biosensor systems for nitrate measurement in water.

Table 8: Types of biological materials, detection systems, LOD and references

Biological materials	Detection system	LOD	Application	Ref.
Methyl viologen/ Nafion/ nitrate reductase (Aspergillus niger)	Conductometric	0.005 mM	Nitrate detection in water	[4]
Carbon nanotube/polypyrrole/nitrate reductase (NaR)	Amperometric	0.17 mM	Nitrate measurement	[27]
Nitrate reductase (NaR)	Cyclic voltammetry	200 nM	Nitrate and nitrite detection	[59]
Escherichia coli	Amperometric	0.1 mM	Nitrate detection in drinking water	[16]

Table 9: Advantages and disadvantages of biosensor systems

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>* Wide linear range of sensor response/detection limit [27,59]</li> <li>*High stability [59,73]</li> <li>*Inexpensive [73]</li> <li>*Small size [74]</li> <li>*Fast response [75]</li> <li>*High selectivity towards targeted ions [59,75]</li> <li>*Portable system</li> </ul>	<ul style="list-style-type: none"> <li>*pH parameter influences the performance of biosensor sensitivity [27,73]</li> <li>*Temperature parameter influences the performance of biosensor sensitivity [73]</li> <li>*Tedious measurement conditions [27,73]</li> <li>*Requirement for sample preparation [27,59,73]</li> </ul>

## VII. FLOW INJECTION ANALYSIS

Flow-based methods for nitrate determination in water were introduced for environmental analytical measurement. This analytical approach is attractive as a good alternative over traditional methods because of high throughput analysis, the low volume of sample and reagent, low cost and it being easy to operate. Hence, flow injection methods can be used as a water quality indicator to monitor parameters such as nitrate in a water sample [38-47].

Generally, there are four main processes in flow injection methods: distribution, reduction, pre-detection, and detection. The distribution process normally uses a pump to carry a sample from the input to the next process with a constant flow rate. The pump in flow injection methods allows the supply of sample continuously within a measurement time frame. A reduction process is the second process in flow injection methods that is introduced for nitrate reduction. The reduction agent works by converting the nitrate ion into an active nitrite ion by activating the nitrate ion property in the sample. After the conversion process is completed, the next process is the pre-detection process. In this process, a detection agent is used to form a compound by reacting the reduction agent with the nitrite ion that was produced previously in the nitrate reduction process. Then, the detection system detects nitrate and nitrite. The most common detection agents are griess-illosvay, acidic hydrogen peroxide, sulfanilamide and N-(1-naphthyl) ethylenediaminedihydrochloride (NED).

Several reduction agents have been introduced to perform nitrate reduction in flow injection methods. The most common reduction agents are zinc column, cadmium column, vanadium (III), titanium (III) chloride and hydrazine sulphate. The selection of the reduction agent is important because an incorrect choice will lead to problems such as excessive time consumption and environmental pollution. Hydrazine [45] need a lengthy reaction time for the reduction process and colour development before detection. Hazardous reagents such as cadmium associated with toxic waste can contribute to pollution after usage [39,40].

Numerous flow injection methods coupled with different types of detectors have been reported for nitrate determination in water samples. Detection systems such as spectrophotometric and chemiluminescence are highly preferred to be employed as detection mechanisms in flow injection applications for nitrate detection. The detection output such as absorbance is proportional to the sample concentration. Such behaviour is described by Lambert's law, where absorbance is proportional to the concentration of measured material or sample.

The maximum output of detection can be achieved by controlling several chemical and physical parameters such as solution pH, flow rate for carrier and sample, sample volume and reaction coil length. These parameters have to be controlled in order to achieve an accurate result, sample throughput, and a maximum peak shape of output. Therefore, optimum parameters are required.

Yaqoob et al. [40] mentioned that the luminal chemiluminescence efficiency is dependent on pH, which demonstrates strong emission via alkaline conditions. pH helps for nitrate reduction. The absorbance or detector response changes significantly by increasing the pH, which helps to develop the azo dye formation efficiently for spectrophotometric detection [39].

Table 10 and Table 11 summarise the optimised parameters from previous investigations and flow injection methods for nitrate detection, respectively. The flow rate of the sample, carrier and reagent solution in flow injection methods are important, as the reaction time can be controlled and adjusted. Hence, flow rate is said to be a critical parameter for time-consuming reactions [41]. Furthermore, the flow rate can enhance the sensitivity as well as high sample throughput [44]. A maximum signal emission such as luminal chemiluminescence [40] can be achieved by using an optimum flow rate. Optimum flow rate helps to stabilise the baseline on the detection area and improve the output such as intensity and absorbance.

Sample volume [39,40] contributes to increased detection capabilities such as luminal chemiluminescence intensity and spectrophotometric absorbance. To find the optimum sample

volume, the volume of the samples was manipulated and the outputs were monitored. The best result in terms of shape peaks of output by specific sample volume is considered as the optimum sample volume.

The optimum reaction coil length in flow injection methods can enhance the measurement of absorbance or intensity [39]. To find the optimum length, the dimensions of the reaction coil are manipulated. The optimisation procedure for reaction coil length is similar to the optimum sample volume selection based on absorbance or intensity output.

Table 11 shows that flow injection methods provide low LOD, rapid measurement, low-cost systems, and are easy to operate. The advantages and disadvantages of flow injection methods are summarised in Table 12. Nevertheless, some disadvantages were identified, such as the use of a hazardous reagent such as cadmium, which is harmful to humans and contribute to environmental pollution. In addition, the interference of other contamination disturbs the detection performance; hence, detection accuracy is degraded. Moreover, tedious sample preparation is required to prepare the sample. Furthermore, the system needs periodical maintenance involving the mechanical parts in the flow injection methods such as the peristaltic pump and injection valve. Hence, the maintenance cost should also be considered.

Table 10: Optimised parameters in flow injection methods

Optimum value					
Detection system	Spectrophotometric [5]	Spectrophotometric [6]	Chemiluminescence [7]	Spectrophotometric [8]	Spectrophotometric [9]
pH	-	7.5	12	7.8	6.5
Flow rate (mL/min)	0.8	2	1.6	1	2.1
Sample volume (μL)	500	150	150	250	100
Reaction coil (cm)	350	200	150	100	30

Table 11: Flow injection methods for nitrate detection

System	Reduction	Detection agent	Detection	LOD	Application	Ref.
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	<b>agent</b>		<b>system</b>			
Flow analysis	Zink granules	N-(1-naphthyl)ethylene diamine (Griess reagent)	Spectrophotometric	1.3 $\mu\text{g/L}$	Nitrate measurement in marine and estuarine waters	[61]
Flow-injection	Cadmium (Cu-cd)	Acidic hydrogen peroxide	Luminolchemiluminescence	0.02 $\mu\text{gN/L}$	Nitrate and nitrite determination in freshwater	[62]
Multi-parametric automated	Cadmium column	Modified griess-ilosvay	Spectrophotometric	0.0207 $\text{mgN/L}$	Nitrate, nitrite and sulfate determination in drinking water and waste water	[66]
Flow-injection	Vanadium (III) chloride	Sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED)	Spectrophotometric	0.1 $\mu\text{M}$	Nitrate and nitrite determination in aqueous samples	[63]
Flow-injection	Cadmium column and sulfanilamide	N-(1-naphthyl)ethylenediamine dihydrochloride (NED)	Spectrophotometric	50 $\mu\text{gN/L}$	Nitrate and nitrite determination in natural waters	[60]
Flow-injection	Cadmium	Sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED)	Spectrophotometric	0.013 $\mu\text{g/L}$	Nitrate, nitrite and ammonium determination in soils	[67]
Flow analysis	Enzymatic assay reagent	Griess-ilosvay	Spectrophotometric	0.73 $\text{mg/L}$	Nitrate and nitrite determination in water	[65]

Table 12: Advantages and disadvantages of flow injection methods

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>*Low LOD [60,62,64]</li> <li>*Simple system [60,62,64]</li> <li>*Rapid measurement [60,66,67]</li> <li>*Low-cost system [60,67]</li> <li>*High throughput [60,62,66,64]</li> <li>*Easy to assemble [60]</li> <li>*Easy to operate [61]</li> <li>*Optimum sensitivity [66]</li> <li>*Good sensitivity [61,66,67]</li> <li>*Good repeatability [66]</li> <li>*Low reagent consumption [60,62,66]</li> <li>*Minimum waste generation [66]</li> <li>*Minimum man power/labour to run the experiment [60,62]</li> </ul>	<ul style="list-style-type: none"> <li>*Exposure to hazardous reagents such as cadmium [60,62]</li> <li>*Interference of other contaminants such as phosphate, Co(11) and Fe(111) [60,62,66]</li> <li>*Tedious procedure for reagent preparation [60,61]</li> <li>*Maintenance of mechanical parts such as pump and valve as the components have a life span</li> <li>*Reproducibility issue of cadmium column over long period usage</li> <li>*The natural behaviour of griess reagent is unstable over a long period usage</li> </ul>

## VIII. ELECTROMAGNETIC SENSOR

### a. Introduction of planar electromagnetic sensor

Currently, various types of impedance-based sensor have been introduced. This type of sensor is suitable for direct measurement [77]. Planar electromagnetic sensor array (PESA) is one type of impedance-based sensor. This sensor reflects the changes of physical quantity of sample based on the changes in electrical impedance. The details of PESAs detection mechanism is discussed in the next subchapter.

Near-to-surface properties such as conductivity, dielectric and permeability of an analyte solution can be determined via PESA. It is reported that PESA has the ability to detect and estimate nitrate in water samples [3,6,7,19,48,49,76].

Many studies have been carried out to enhance the sensor performance in terms of sensitivity by optimising the sensor design or configuration. It is convenient to use PESA for in situ



measurement system. Moreover, PESA is also highly durable, has a fast response, and is low cost. The advantages and disadvantages of PESA are summarised in Table 13.

Table 13: Advantages and disadvantages of PESA

Advantages	Disadvantages
*Low cost [3,6,7,19,43,44,69–71]	*Requires algorithm for sample classification [19]
*Convenient [3,6,7,19,43,44,69–71]	*Needs regular maintenance before experiment
*Suitable for in situ measurement systems [3,6,7,19,43,44,69–71]	*Requires a wide range of frequency to determine the resonant frequency
*Highly durable [3,6,7,19,43,44,69–71]	
*Rapid reaction [3,6,7,19,43,44,69–71]	

A novel planar electromagnetic sensor and thorough study were considered for nitrate detection in aqueous water [6,7]. Two samples such as sodium nitrates and ammonium nitrates were used to study the sensor behaviour [7]. The best sensor was determined by investigating the sensor performance based on two arrangements: series connection and parallel connection. The proposed sensors consist of a mender sensor and interdigital sensor. This combination formed an electromagnetic sensor.

This finding demonstrates that the series connection gives better nitrate detection than parallel connection in terms of sensitivities. Therefore, the authors recommended to use the series configuration for electromagnetic sensor development. The improvement of the detection can be effected by focusing on the sensor material. The authors suggest using the gold material as a sensing element for electrode development. The nitrate ion has the characteristic of being attracted to gold. Hence, most nitrate ions present in water can be detected. The use of substrates with high dielectric constant can improve the sensor's sensitivity. The penetration of the sensor's electric field on the other side occurs by means of a low dielectric constant substrate, which decreased the sensitivity. Therefore, a high dielectric constant substrate is a must for developing a high-sensitivity sensor.

Further optimisation of planar electromagnetic sensors has been carried out in order to determine the best sensor with the highest sensitivity [7]. Three types of configurations: parallel, star and delta, have been studied. The proposed sensors consist of a mender sensor and an interdigital

sensor that are connected in series. A mender sensor is based on five loops of coils. The interdigital sensor is designed based on a consecutive positive electrode and negative electrode.

A simulation using COMSOL Multiphysics 4.2 software has been carried out to evaluate the sensitivity of all configurations based on impedance changes. Hence, the best sensor in term of the highest sensitivity can be determined. The frequency for the simulation is varied from 1–24 MHz. Three parameters have been considered: conductivity  $\sigma$ , permittivity  $\epsilon$ , and permeability  $\mu$ . The results demonstrate that all configurations are sensitive to the material properties. Based on the simulation data, the best sensor that is highly sensitive to nitrate ions is the star configuration. Nor et al. [7] validated the simulation results through experiments. Both the simulation and experimental results are in good agreement.

Multivariate statistical tools associated with a planar electromagnetic sensor are useful for real-time measurement in estimating and classifying the nitrate concentration level in water. Such tools are independent component analysis (ICA) [19,69] and artificial neural networks (ANN) [7]. These tools enhance the capability of planar electromagnetic sensor to differentiate the nitrate contaminant level presence in water. Hence, the accuracy of the detection is improved. Generally, the indicator to determine the performance of ICA and ANN is based on the root mean square error (RMSE) value.

Yunus et al. [19] applied the ICA model for nitrate estimation in natural water. The proposed ICA model is tested using eight sets of samples that contain a mixture of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium phosphate ( $\text{NH}_4$ )<sub>2</sub>HPO<sub>4</sub>. They proposed three components in the analysis: the fixed point algorithm, spectral matching and contamination calculation. A second derivative equation is applied to the output sensitivity of mixing samples in order to differentiate the sample's data trends significantly. Hence, the identification of nitrate based on concentration level can be easily carried out. The ICA model is able to detect nitrate contamination in distilled water as well as differentiate the concentration level with a correlation coefficient of 0.9921. A large error is observed when the concentration is less than 15.3 mg/L, while low error is obtained at high concentrations. This finding indicates that the ICA model is a trustworthy multivariate-statistical tool for nitrate estimation in water. On the other hand, the ICA model requires repeating measurements in order to obtain sufficient data for nitrate estimation. Hence, the estimation process of ICA is time-consuming as a number of measurements are compulsory.

Therefore, as an alternative, the ANN estimation tool has been introduced to overcome this problem.

The ANN approach has been used [7] to estimate nitrate contamination presences in water samples. The proposed ANN model is subjected to a nitrate sample in the form of  $\text{KNO}_3$  and  $\text{KNO}_4$ . Nitrate concentrations vary from 5–114 mg and were dissolved in 1 L of distilled water. To confirm the estimation ability of the proposed ANN, seven sets of mixed  $\text{KNO}_3$  and  $\text{KNO}_4$  with different levels of concentrations dissolved in water were prepared and tested. The finding demonstrates that the proposed ANN model can detect and estimate the nitrate concentration in distilled water with an RMSE of 0.0132. To validate the capability of the ANN model in estimating nitrate concentration, the proposed ANN model is removed from the system and the output is observed. The result demonstrates that RMSE value increased significantly to 0.0977. Therefore, the application of proposed ANN model is beneficial and crucial for nitrate estimation in water.

#### b. Planar electromagnetic detection mechanism and equivalent circuit

PESA consists of a series-connected meander sensor and interdigital sensor [49]. The sensor array is fabricated in thin substrate such as printed circuit board (PCB) using a conventional PCB fabrication technique. The meander sensor consists of several loops or coils of electrodes and is designed to be spiral or square in shape. The interdigital sensor consists of positive and negative electrodes and is designed to be parallel between positive and negative electrode. The ground electrode is placed at the bottom of the interdigital sensor. The architecture of the electromagnetic sensor is illustrated in Figure 3.

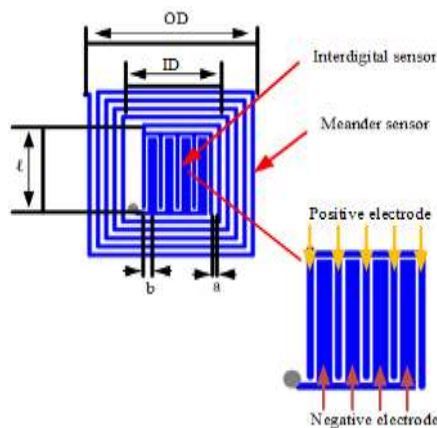


Figure 3: Electromagnetic sensor architecture

As reported in [48,50], the sensor's response in terms of strong current signal can be improved by widening the negative electrode dimension of the interdigital sensor [51]. Significant changes on impedance occurred by altering the shape and geometric parameters of the interdigital electrode. For example, [52] mentioned that the impedance of water bulk medium increases with the distance between the two electrodes and decreases by increasing the area of the electrode. Therefore, the total impedance of the sensor is increased as the wide distance configuration applies for the electrodes.

The inductance from a meander sensor could also influence the performance of the planar electromagnetic sensor. The inductance equation of the mender sensor can be expressed as [53,54]:

$$L = 1.39 \times 10^{-6} (OD + ID) N_L^{5/3} \log_{10} \left( 4 \frac{OD + ID}{OD - ID} \right) \quad (1)$$

Where L represents the inductance of a mender sensor (Unit: Henrys), and  $N_L$  is the number of inductor turns. OD and ID are the outer and inner diameters, respectively, of the inductor respectively (Unit: meters). A coil structure or inductive part in the planar electromagnetic sensor plays a very important role where it helps to weaken the capacitance of the measured medium. Hence, the capacitive impedance will definitely change to inductive impedance at high frequencies. Therefore, the measurement accuracy is improved as the capacitive part of the total impedance normally interferes with the measurement precision. Furthermore, weakening the capacitance caused by the inductance from coil structure will decrease the medium impedance. Hence, the current flow in the medium is increased as the total impedance decreases. As a result, the measuring error is reduced as the measuring current increases [53].

The measured resonant frequency and the zero reactance frequency from an experiment are very important to determine and estimate the real, imaginary, and complex permittivity of a medium. The resonant frequency is defined as the frequency in which the maximum impedance amplitude of the real part of a medium is observed. The zero reactance frequency is the frequency of the imaginary part of a medium where the impedance value is zero. On the other hand, these

frequencies change with the concentration of the measured medium, which in turn allows the calculation of concentration. Moreover, these frequencies are reported to be highly dependent on the inductance and capacitance of the planar electromagnetic sensor array [53].

An investigation on the relationship between capacitance and conductivity of a medium based on electromagnetic sensor configuration, coating layer and water solution has been carried out [54]. The protective layer known as the coating layer insulates the sensor surface from direct exposure to water solution. The protective layer protects the sensor surface from extreme chemical reaction that comes from contaminants. Hence, the use of a protective layer can avoid the sensor from being damaged. Moreover, a protective layer acts as a constant capacitance known as a double-layer capacitor,  $C_{dl}$ .  $C_{dl}$  is highly dependent on copper line surface area and the thickness of coating layer [54]. A charge transfer resistor,  $R_{ct}$  is the resistor that is present in the coating area. This resistor is connected in parallel with  $C_{dl}$  as illustrated in Figure 4. Psychochemical variables such as electrical potential and chemical potential have the ability to charge the interface and allow the transportation of reacting species between the water bulk solution and interfacial reaction zone. Therefore, the psychochemical variables make  $R_{ct}$  be influenced by their existence in the water bulk medium.  $R_E$  and  $C_E$  are the resistance and capacitance of water bulk, respectively.

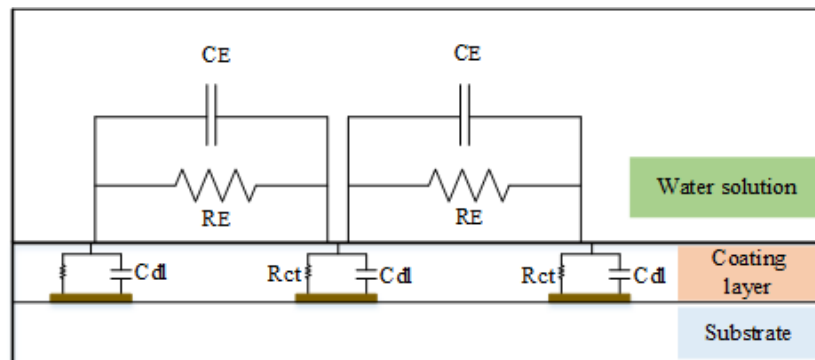


Figure 4: Physical representation based on planar electromagnetic sensor configuration

The dielectric properties of a water solution arise from the influence of an external electric field of planar electromagnetic sensor on the dielectric dipole and mobile ions. When the water solution is subjected to an external electric field, the neutralisation or polarisation process of dipoles occurs. As a result, the dipole is re-aligned by shifting its equilibrium positions, where a

positive charge is displaced toward the field of a negative charge and vice versa for a negative charge. Another significant dipole realignment is the formation of an internal electric field between the dipoles. This re-alignment process is different for different types of materials. Hence, the magnetic response of each material across the frequency spectrum is unique. The dipole re-alignment process is illustrated in Figure 5.

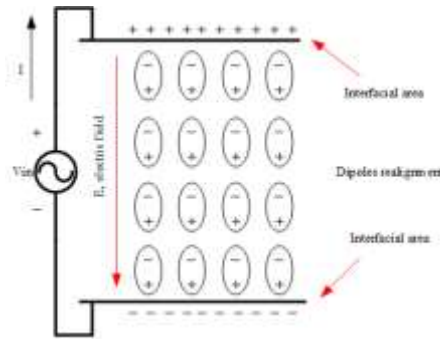


Figure 5: Dipole realignment process

Figure 5 shows the realignment process of dipoles. In the bulk liquid area, dipole re-alignment from the separation of charge in the monomers making up the material builds up capacitance  $C_E$  of the liquid solution. As a result, a charged surface is formed at the interfacial area. Hence,  $C_{dl}$  is formed in the interfacial area. This is known as an electrical double layer (EDL) [52].

Mobile ions must be considered as well. Mobile ions are present in water due to contamination. Conductive current movements in the water bulk area are based on the flow of mobile ions when subjected to an external electric field. Hence, the resistance of water bulk,  $R_E$  is highly dependent on the strength of the applied external electric field. Ion movement is dependent on the viscosity of the medium: it moves faster in the lower viscosity medium and moves slower in a higher viscosity medium. On the other hand,  $R_{ct}$  is based on the kinetics of absorbed or desorbed of mobile ions in the interfacial layer [52].

The equivalent circuit of the planar electromagnetic sensor based on a series-connected meander sensor and interdigital sensor is presented in Figure 12. The equivalent circuit shows the sensor's impedance, which consists of  $C_{dl}$ ,  $R_{ct}$ ,  $C_E$  and  $R_E$ . The constant parasitic capacitor is denoted as  $C_C$ . The equivalent circuit of PESA can be expressed as follows:

$$Z = j\omega L + \frac{\frac{1}{j\omega C_C} \left( \frac{R_E}{1 + R_E j\omega C_E} + \frac{R_{ct}}{1 + R_{ct} j\omega C_{dl}} \right)}{\frac{1}{j\omega C_C} + \left( \frac{R_E}{1 + R_E j\omega C_E} + \frac{R_{ct}}{1 + R_{ct} j\omega C_{dl}} \right)} \quad (2)$$

The relationship between the permittivity and conductivity with the sensor's geometrical constant will enable the calculation of the permittivity and conductivity of every water sample using a proper fitting function. Based on Equation (2), the real part of conductivity,  $\sigma$  can be estimated from Equation (3), while relative permittivity  $\epsilon'_r$  is estimated from Equation (5) [53].

$$\sigma = \frac{1}{kR_E} \quad (3)$$

where  $k$  is the geometrically correlated constant of the interdigital sensor, which is defined as in Equation (4) [53], and  $R_E$  is the resistance of bulk liquid solution.

$$k = \frac{\ell(N_C - 1)K[(1 - (a/b)^2)]^{1/2}}{2K[a/b]} \quad (4)$$

Where  $\ell$ ,  $a$ , and  $b$  are the interdigital sensor dimensions as shown in Figure 3 while  $N_C$  is the number of interdigital electrodes.

$$\epsilon'_r = \frac{C_E}{k\epsilon_o} - \epsilon_s \quad (5)$$

Where  $\epsilon_o$  and  $\epsilon_s$  are the free space permittivity and relative permittivity of substrate respectively.  $C_E$  is the capacitance of bulk liquid solution, calculated based on Equation (6) [52]:

$$C_E = \frac{\epsilon'_r \epsilon_o A}{d} \quad (6)$$

Where  $A$  is the electrode geometry of area  $A$  in which current is carried, and  $d$  is the thickness of the sample between electrodes. The imaginary part of complex permittivity of the medium,  $\epsilon''_r$  can be expressed as:



$$\varepsilon_r'' = \frac{1}{kR_E \omega \varepsilon_0} \quad (7)$$

Where  $\omega$  is the radian frequency (Hz). The complex permittivity of a medium,  $\varepsilon_r''$  shows an inverse relationship between  $R_E$  and  $\omega$ . Therefore, increasing the radian frequency should decrease its complex permittivity.

#### c. Selective membrane for PESA detection improvement

Various methods have been introduced for water contamination treatment such as flocculation, floatation, ferric hydroxide and filtration. However, these conventional methods have their own drawbacks that restrict their applications, such as requiring pre-treatment process and reagent needing to be consumed during the operation. Furthermore, these methods are not economical for the treatment of large-scale samples with high concentration.

Currently, membrane technology has gained great attention in sensing technology. Most workers nowadays like to integrate membranes or known as conducting polymer, into their sensor system in order to improve the sensing performance [78]. Polymers have gained tremendous recognition in the field of liquid and gas sensing. This so called ‘an active layer’ has been introduced since 1980s. It is reported that the conducting polymer has various improved characteristic. Such characteristic are highly sensitive and short response time. Moreover, their fabrication process is not complicated which easy to synthesize via electrochemical process [79].

Yunus et al. [3] applied the membrane technology into a planar electromagnetic sensor array. The proposed membrane is inexpensive, as no additional reagent is required for the pre-treatment. Hence, this is an alternative method to save costs. The proposed membrane consists of a combination of polymer dope modified silica (polymer) and N-Methyl-2-pyrrolidone (NMP) (solvent). Poly-sulfone (PSF) and modified silica were selected to represent the polymer material in the membrane to enhance the selectivity towards nitrate ions. The organic compound NMP was employed as the main element of the membrane, where it has five-membered lactams.

This finding demonstrates that the average sensitivity of a planar electromagnetic sensor varied from 0.007–223 % via experiments using nitrate concentrations of 5 ppm, 25 ppm, and 100 ppm. The proposed membrane enhanced the sensor response in terms of sensitivity and selectivity towards nitrate ions.

## IX. CONCLUSION

The aim of this study was to consider the various ways that the enhancements of knowledge and material sciences have played a prominent and relevant role in improving nitrate detection capability. The improvement may come from the introduction of a suitable membrane into a sensor system, sensor modification via design and configuration, system miniaturisation, the selection of electrode material for sensor development, techniques to improve bonding between membrane and sensor, and minimising the environmental impact during measurement.

The drawbacks of conventional methods such as system limitations have been highlighted. Even though most conventional methods provide sufficient results for nitrate ions detection, they are generally time-consuming, immobile (i.e. laboratory-based), and the measurement is not performed routinely.

In summary, planar electromagnetic sensors have become popular in pollutant determination due to their non-destructive measurement, low cost, high performance features such as fast response, and simple operation. Extensive research on membrane development is crucial in order to enhance the sensor performance in terms of selectivity and sensitivity.

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